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Correlation of Calculated Halonium Ion Structures with Experimental Product Distributions from Terminal Alkenes: The Effect of Electron-Withdrawing Fluorine Substituents on the Structure and Charge Localization of Halonium Ions.

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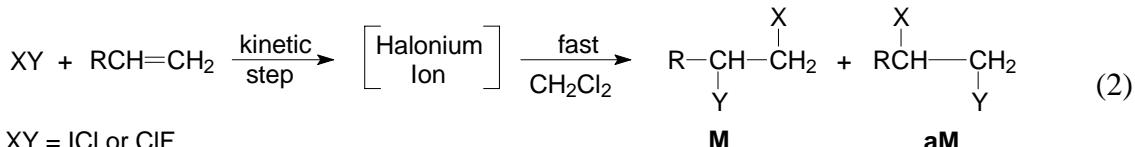
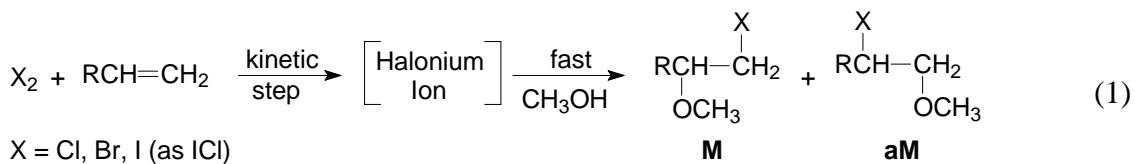
ABSTRACT

The structures and charge densities of halonium ions derived from addition of halogen electrophiles to fluorosubstituted terminal alkenes were computed using quantum chemical methods. Geometry optimizations were performed at the second-order perturbation theory level (MP2, also known as MBPT(2)), using the Spartan02 program and also at the density functional theory level, using the GAMESS quantum chemistry code with the B3LYP hybrid functional. An additional set of B3LYP calculations incorporating the Polarizable Continuum Model (PCM) to probe methanol solvent effects was also performed. The halonium ions from terminal fluoroalkenes were found to be symmetrical (**C**), unsymmetrical **B** or **D**, or open-ions described by **A** or **E**. These calculated data support experimental product distributions and they can predict the product regiochemistry from halonium ions opened by anions in aprotic solvents or when

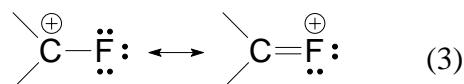
opened by protic solvents like methanol. Electron-withdrawing alkyl groups tend to decrease the S_N1 -character of the product-determining ring-opening transition state, and an S_N2 -like process occurs which is more susceptible to steric effects.

Introduction

Recently we reported on the symmetry of halonium ions from ionic reaction of chlorine (Cl_2), bromine (Br_2), and the interhalogens iodine monochloride (ICl) and chlorine monofluoride (ClF) with terminal alkenes.¹⁻⁵ The product regiochemistry, Markovnikov **M** or *anti*-Markovnikov **aM**, is determined by the fast-step. Our study reported that the **M/aM** product distribution was greatly influenced by the symmetry of the halonium ions; and that the halonium ion symmetry was changed dramatically by fluorine substitution.¹ Regiosomers from Cl_2 and Br_2 were obtained from their solvent incorporated products in methanol as shown below. All ClF reactions with terminal alkenes were carried out in methylene chloride as solvent.

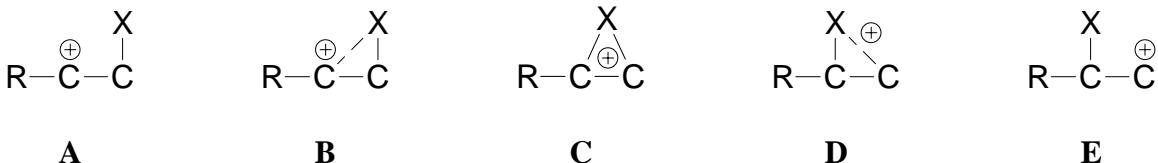


Substituting a vinyl hydrogen with a fluorine presents an interesting situation for electrophilic reactions. The π -bond is less reactive toward electrophiles due to the electron-withdrawing effect of the vinyl fluorine. Therefore, carbocations or radical cations are destabilized by fluorine and the intermediates are difficult to generate. When the ionic intermediate is formed, it can be stabilized by back-bonding from the lone pair (2p) electrons on the fluorine.



A vinyl fluorine alters the shape of the halonium ion intermediate and the **M** to **aM** product distribution. The **M** to **aM** product ratio was also greatly influenced by the alkyl substituent on

the terminal alkene. A structure for the halonium ion intermediate was assigned on the basis of the **M/aM** ratio as either **A**, **B**, **C**, **D**, or **E**.¹



In this paper we utilize quantum chemical calculations to probe the bond distance, bond angles and charges on substituted terminal halonium ions. These calculated data are correlated with our assigned structures (**A** → **E**) of halonium ions from regiochemical product distributions (**M/aM** product ratio¹). Geometry calculations have been performed by others⁶⁻¹¹ but little has been done to investigate asymmetrical bridged structures. While Sordo¹⁰ proposes that a tightly bridged structure is energetically unfavorable, others^{7,8} show they are the preferred structures.

Methods

Geometry optimizations were performed at the second-order perturbation theory level (MP2, also known as MBPT(2))¹², using the Spartan02 program and also at the density functional theory level, using the GAMESS¹³ quantum chemistry code with the B3LYP hybrid functional¹⁴, which included the VWN5 correlation functional¹⁴. In addition, a separate set of B3LYP calculations incorporating the Polarizable Continuum Model (PCM)¹⁵ were performed to probe the methanol solvent effects. The 6-311++G(d,p) basis set¹⁶ was used for all calculations. Other work has shown the necessity for diffuse and polarization basis functions^{11,17} which we have used in our study. There was no attempt made to quantify the sensitivity of predicted geometries to the choice of basis set. Harmonic vibrational frequencies were calculated at the B3LYP and B3LYP+PCM levels for each structure to ensure that the optimized structure is

indeed a local minimum on the ground state potential energy surface. Unless otherwise noted, $R = \text{CH}_3$ and $R_f = \text{CF}_3$.

The product ratios were determined experimentally and reported previously.^{1,2} For experimental reactions, side chains were generally longer than those used for calculations (CH_3^- and CF_3^-) reported in Table 1.

Results and Discussion

Table 1 contains the $X-\text{C}_1-\text{C}_2$ and $X-\text{C}_2-\text{C}_1$ bond angles from calculations obtained using the B3LYP/6-311++G(d, p) PCM method, which includes corrections for the solvent methanol. The $X-\text{C}_2-\text{C}_1$ bond angles from the B3LYP/6-311++G(d, p) and MP2/6-311++G(d,p) calculations, which do not include corrections for solvent, are also included in Table 1.

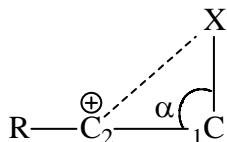
Halonium ion structures of **A** through **E**, assigned from the calculated structures and also independently assigned from our experimental data^{1,2} are in Table 1. Where experimental data are lacking, we predict the halonium ion structure in Table 1. These calculated data provide a more refined structure for the halonium ion than we were able to predict based on experimental data.^{1,2}

Refined Structures Defined

The $X-\text{C}_1-\text{C}_2$ bond angle is best suited for assigning structures **A** and **B** while the $X-\text{C}_2-\text{C}_1$ bond angle is used for structures **D** and **E**. For example, a $X-\text{C}_1-\text{C}_2$ bond angle of 90 degrees or more is assigned structure **A** while a $X-\text{C}_1-\text{C}_2$ bond angle (α) of 75 to 80 degrees represents structure **B**. Bond angles of 85 to 90 degrees describe halonium ions as resembling **A** but approaching structure **B**, and 80 to 85 degrees like structure **B** but becoming like structure **A**; this is denoted

as **A** \Rightarrow **B** and **B** \Rightarrow **A**, respectively. A bond angle α of 75 to 80 degrees represents structure **B**; 70 to 75 degrees as **B** \Rightarrow **C**, and 65 to 70 degrees as **C** \Rightarrow **B**. Symmetrical structure **C** is represented by 55 to 65 degrees for either the X–C₁–C₂ or X–C₂–C₁ bond angles. Similarly, a X–C₂–C₁ bond angle of 90 degrees or more represents structure **E**, 85 to 90 **E** \Rightarrow **D**, 80 to 85 **D** \Rightarrow **E**, 75 to 80 **D**, 70 to 75 **D** \Rightarrow **C**, 65 to 70 **C** \Rightarrow **D**, and 55 to 65 as the symmetrical structure **C**. These refined structures could not be gleaned from our experimental data.^{1,2}

Bond Angles



$$\alpha > 90^\circ \mathbf{A}$$

$$\alpha > 85^\circ\text{--}90^\circ \mathbf{A} \Rightarrow \mathbf{B}$$

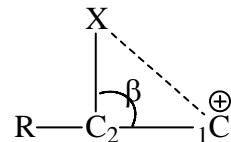
$$\alpha > 80^\circ\text{--}85^\circ \mathbf{B} \Rightarrow \mathbf{A}$$

$$\alpha > 75^\circ\text{--}80^\circ \mathbf{B}$$

$$\alpha > 70^\circ\text{--}75^\circ \mathbf{B} \Rightarrow \mathbf{C}$$

$$\alpha > 65^\circ\text{--}70^\circ \mathbf{C} \Rightarrow \mathbf{B}$$

$$\alpha \text{ or } \beta \text{ } 55^\circ\text{--}65^\circ \mathbf{C}$$



$$\beta > 90^\circ \mathbf{E}$$

$$\beta > 85^\circ\text{--}90^\circ \mathbf{E} \Rightarrow \mathbf{D}$$

$$\beta > 80^\circ\text{--}85^\circ \mathbf{D} \Rightarrow \mathbf{E}$$

$$\beta > 75^\circ\text{--}80^\circ \mathbf{D}$$

$$\beta > 70^\circ\text{--}75^\circ \mathbf{D} \Rightarrow \mathbf{C}$$

$$\beta > 65^\circ\text{--}70^\circ \mathbf{C} \Rightarrow \mathbf{D}$$

Comparing the Models

Table 2 contains bond lengths from the B3LYP calculations, both with and without corrections for solvent, and Table 3 summarizes the MP2 bond lengths. Table 4 lists the atomic charges from the B3LYP+PCM and MP2 calculations.

The MP2 and B3LYP C₁-C₂ computed bond lengths are in excellent agreement, with differences of at most 0.02 Å. Inclusion of solvent effects via the B3LYP+PCM method has a small effect on the C₁-C₂ bond lengths, which differ from the B3LYP values by at most 0.01 Å. However, the predicted C₁-X and C₂-X bond lengths are more sensitive to the theoretical method than are the C₁-C₂ bond distances. In general, the incorporation of solvent effects using the PCM method has minor effects on the halonium ion bond angles (Table 1), bond lengths (Table 2), and charge densities (Table 4) relative to the corresponding predictions in the gas phase.

Experimental predicted structures and calculated geometries are identical where carbocations with mono-coordinated halonium ions (i.e., having structures **A** or **E**) are anticipated (Table 1, structure **A** Runs 3 and 13; structure **E** Run 12 for chlorine, the perfluoroalkene in Run 12 did not react ionically with bromine). The calculated structures, including those corrected for solvent, are generally more symmetrical than the **B** and **D** structures predicted from experimental data^{1,2} (Table 1, Runs 1, 2, 7, 9 for chlorine). Halonium ions formed from alkenes with a fluorine on both carbon-1 and carbon-2 (Table 1, Runs 11 for chlorine, and Runs 14 and 15) gave calculated structures less symmetrical than what we predicted based on experimental data.^{1,2}

The MP2, B3LYP, and B3LYP+PCM data in Table 1 overall are in good agreement. In those instances where they disagree (Runs 3, 5 and the bromonium ions from Runs 4 and 9), the B3LYP and B3LYP+PCM results are generally similar to each other but distinct from MP2. An exception is the bromonium ion case from Run 12, in which case the MP2 and B3LYP+PCM predictions are similar but in slight disagreement with B3LYP. However, these differences are

typically small and the overall level of consistency between the three theoretical methods lends confidence to their reliability.

Trends

Structures for the halonium ions **A** through **E** were assigned from $X-C_1-C_2$ and $X-C_2-C_1$ bond angles. These assignments are generally supported by bond lengths (Tables 2 and 3) and charge densities (Table 4). Halonium ions assigned unsymmetrical structures **A** (Runs 3, 5, 6, 13, 14 and 15) have shorter C_1-X than C_2-X bond lengths (see Tables 2 and 3), except for the MP2 predicted geometries of the bromonium ions in Runs 6 and 15, in which the C_1 -Br bond lengths are slightly longer than C_2 -Br. Furthermore, the positive charges are greater on carbon-2 than carbon-1 (Table 4), with the sole exception of the bromonium ion in Run 5, for which the B3LYP+PCM Löwdin atomic charge of C_1 exceeds that of C_2 . In Runs 1, 2, and 9, in which the assigned halonium ion structure is nearly symmetrical like **C**, the predicted C_1 -X bond lengths are smaller than C_2 -X (except for X=Br in Run 2). In contrast, the C_1 -X bond lengths are larger than C_2 -X in the nearly symmetrical halonium ions in Run 7. The PCM Löwdin atomic charges on carbons -1 and -2 of the symmetrical ions (Runs 1, 2, 7, and 9) differ by less than 0.1 electron (although in the instance of the chloronium cation in Run 1, the difference in charges on C_1 and C_2 is 0.39 electron.) In contrast, the MP2 natural population analysis charges on C_1 and C_2 in the nearly symmetrical halonium ions show considerable more variation than the corresponding B3LYP+PCM Löwdin atomic charges. Unsymmetrical structures like **D** or **E** (Runs 4, 8, 10, 11, 12) have the positive charge primarily on carbon-1 (Table 4) and C_1 -X bond lengths which are shorter than C_2 -X. The chlorine and bromine atoms in all of the halonium ions have positive charges, except in the case of the MP2 natural population analysis charges for Run 5 (see Table

4). Atomic charges and the C₁-X, C₂-X relative bond lengths are generally consistent with the structural assignments based upon the X-C₁-C₂ and X-C₂-C₁ bond angles, which provide the most reliable correlation with experimental data.

Structures

I. Hydrocarbon Substituents (R=alkyl):

(a) No Vinyl Fluorines on Carbons 1- or -2.

The halonium ion geometries from the PCM calculations on the hydrocarbon alkene propene (Table 1, Run 1) have an X-C₂-C₁ bond angle consistent with structure **C** and an X-C₁-C₂ bond angle more like **B**. The X-C₂ bond is longer than the X-C₁ bond at all computational levels (Tables 2 and 3, Run 1), which indicates some asymmetry toward **B**. In Run 1, carbon-1 is more positively charged than carbon-2, except for the B3LYP+PCM bromonium ion. Our calculations indicate a slightly more symmetrical intermediate (**C** from X-C₂-C₁ bond angle and **B** from X-C₁-C₂ bond angle, Table 1) than that predicted by experimental product ratios (**B**, Table 1). Throughout this study we find that calculated structures tend to be slightly more symmetrical than those inferred by experimental data in solution.

The hydrocarbon vinyl ether halonium ions have X-C₁-C₂ bond angles of 100 degrees and X-C₂-C₁ around 40 degrees, consistent with an open-ion **A** (Table 1, Run 13). Bond lengths (X-C₂ > X-C₁) and the positive charge on carbon-2 support the open-ion structures (Tables 2, 3 and 4).

(b) With One Vinyl Fluorine on either Carbon -1 or -2

Halonium ions from a terminal alkene with a single fluorine on the number-2 carbon have a small $X-C_2-C_1$ angle ($\beta < 56^\circ$), where the halogen (X) is more closely associated with the terminal carbon (Table 1, Run 3). Therefore the $X-C_1-C_2$ (α) bond angle is a better model than the $X-C_2-C_1$ (β) angle to predict the intermediate, and the open-ion **A** is indicated, although the MP2 geometry is more consistent with the symmetrical structure **C**. The open-ion is supported by bond length and charge distributions (Tables 2, 3 and 4, Run 3). Experimentally, exclusive formation of Markovnikov products in methanol as solvent also support an open-ion intermediate¹ **A** (Table 1, Run 3). We suggest that halonium ions from terminal alkenes with a single fluorine on the number-2 carbon are unsymmetrical and open-ion intermediates.

A single fluorine on the terminal carbon (Table 1, Run 2) makes the halonium ion more symmetrical as the $X-C_1-C_2$ and $X-C_2-C_1$ bond angles are *ca.* 70° which suggest structure **C** \Rightarrow **D**. Charge distribution (Table 4, Run 2) data show that more positive charge is concentrated on carbon-1 than carbon-2. Our experimental data were best described by the unsymmetrical halonium ion **D** (Table 1, Run 2). The calculated geometry is more symmetrical than intermediate **D** and is best described as **C** with some asymmetry associated with **D** (Table 1, Run 2). The positive charge density on carbon-1 (Table 4, Run 2) supports the formation of predominately or exclusive *anti*-Markovnikov products in methanol as solvent.¹ We suggest that gas phase reactions of 1-fluoroterminal alkenes with interhalogens will give predominately **aM** products primarily due to the positive charge density on carbon-1 (Table 4, Run 2). The bond length C_1-X and C_2-X data are similar and suggest a rather symmetrical intermediate, while

slightly asymmetric structures (**C**⇒**D**) are indicated and supported by charge densities and bond angles (Tables 4 and 1, Run 2).

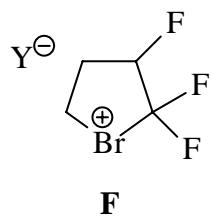
c. With Two Vinyl Fluorines. 1,1- or 1,2-Difluoroterminal Alkenes.

Two fluorines on the terminal carbon give X–C₂–C₁ bond angles of 83 to 95° (Table 1, Run 4) which places the halogen almost directly above carbon-2. The X–C₂ bond is shorter than the X–C₁ bond (Tables 2 and 3, Run 4), and the positive charge on carbon-1 is high (Table 4, Run 4) which supports intermediate **E** for the chloronium ion and **E**⇒**D** for the bromonium ion. It is well known that bromine bridges better than chlorine^{1,18} and that is confirmed by both B3LYP and B3LYP+PCM calculations, but not by MP2. The positive charge on carbon-1 may induce the lone-pair electrons on both fluorines to back-bond as indicated by the shorter C₁–F bond length and decrease in negative charge on the fluorines (compare the C–F bond lengths in Table 2, Run 4 with Run 3, and the charges on fluorine Table 4, Run 4 with Run 3). We did not treat any 1,1-difluoroterminal alkenes with halogens in our earlier paper¹ but it is clear from these calculations that only *anti*-Markovnikov products would be expected from an open-ion **E**.

Placing a fluorine on carbon-1 and on carbon-2 (Table 1, Run 5) moves the halogen closer to the terminal carbon as indicated by the B3LYP+PCM X–C₁–C₂ bond angles of 93°. The larger X–C₂ bond length compared to X–C₁, also supports a structure like **A** (Table 2, Run 5). The positive charge is greater on carbon-2 than carbon-1 and the negative charge of the fluorine on carbon-2 is less than carbon-1 (Table 4, Run 5). We did not react a 1,2-difluoroalkene with halogens in our earlier study¹ but these data suggest that Markovnikov products would be expected from an intermediate like **A** (Table 1, Run 5).

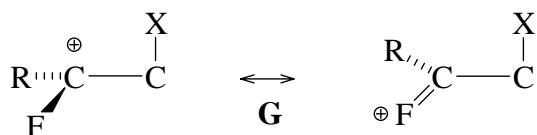
(d) With Three Vinyl Fluorines. 1,1,2-Trifluoroterminal Alkenes.

The structure of the halonium ions are best represented by **A** when all the vinyl hydrogens are substituted for fluorines (Table 1, Run 6). The halogens are above carbon-1 as evidence by the 95 to 100° bond angles, and structures like **A** are also supported by the longer bond length of the X–C₂ compared to X–C₁ bond (Table 2, Run 6). Note, however, that the MP2 bromonium ion geometry is more symmetrical (**E** \Rightarrow **D**). Although we did not experimentally carry out halogenation of an exact model for Run 6, we did reactions with the alkene in Run 15 and we have experimental data for that compound. The calculated data for Runs 6 and 15 (Tables 1, 2, 3 and 4) are similar and support an open-ion **A** (except for the MP2 prediction for the bromonium ion, as previously noted). Our experimental data (Table 1, Run 15) for chlorination and bromination show that significant *anti*-Markovnikov products are formed and that the **M/aM** product ratios are more consistent for a symmetrical structure like **C**. We explained the large amount of **aM** products as evidence for neighboring group participation of the number-4 bromine to form five-membered ring tetramethylenebromonium ion intermediates (**F**).¹



The ability to predict regiochemical product distributions from a calculated three-membered halonium ion is apparent. However, experimental data for the bromination of 4-bromo-1,1,2-trifluorobutene-1 in methanol was not consistent with these calculations.¹ We looked back at our experimental data and noticed that the amount of **aM** product we reported¹

was overstated since 1,3,4-tribromo-3,4,4-trifluorobutane, the major product, trailed into the **aM** peak. These two products, the dibromo addition product and the **aM** bromomethoxy product, could not be resolved by capillary gas chromatography. The **M/aM** ratio of 1/1.3 in Table 1 (Run 15 for bromination) was obtained by ^{19}F NMR integration. Our earlier reported value of 1/6.5 suggested structure **C**.¹ Our calculated data support structure **A** for Runs 6 and 15 and we speculate that the five-membered tetramethylene halonium ion in Run 15 plays a lesser role in this sequence than we described earlier.¹ Thus, a hydrocarbon substituent and a fluorine on the number-2 carbon (Table 1, Runs 3, 5 and 6) support open-ion intermediates like **G**. Halonium



ions from 4-halo-1,1,2-trifluoro-1-butenes are special cases which we are continuing to study.

II. Perfluorocarbon Substituents (R=Perfluoroalkyl).

Changing the hydrocarbon alkyl group of a terminal alkene to a perfluorocarbon destabilizes positive charge on carbon-2. In fact carbon-2 is generally negative (Table 4, Runs 7, 8, 10 and :B3LYP+PCM for Run12) unless the carbon-2 contains a fluorine (Table 4, Runs 9 and 11), a hydrocarbon (Run 15), or a perfluoroether moiety (Run 14). The positive charge on the chlorine and bromine is increased (Table 4, Runs 7 through 12) when a perfluoroalkyl replaces a hydrocarbon alkyl group of a terminal alkene.

(a) No Vinyl Fluorines on Carbons 1- or 2.

Calculations on a terminal alkene with a fluorocarbonalkyl and no vinyl fluorines (Run 7) Table 1) show that the halonium ions are somewhat symmetrical by the $X-C_2-C_1$ and $X-C_1-C_2$ bond angles. The similar $X-C_2$, $X-C_1$ bond lengths are also consistent with a symmetrical

halonium ion (Tables 2 and 3, Run 7). The positive charge now resides primarily on the chlorine or bromine (Table 4, Run 7). Experimentally 1H,1H,2H-perfluoroalkenes react slowly,³ and the inability of carbons 1 and 2 to support positive charge is consistent with the sluggish nature of these alkenes toward electrophiles (Table 4, Run 7). Our earlier experimental data¹ support the unsymmetrical halonium ion **D** for this reaction (Table 1, Run 7). We now believe that more symmetrical intermediates are indicated (**C** \Rightarrow **D** or **D** \Rightarrow **C**). The *anti*-Markovnikov products are best accounted for by an S_N2-like ring-opening of the halonium ion at the sterically least hindered carbon-1. Ring-opening of normal halonium ions in the fast product-determining step by a nucleophile or solvent represents an S_N2-reaction with much S_N1 character because of the positive charge localized on the carbon atoms. In alkenes with electron-withdrawing substituents like the model in Run 7, the positive charge is on the chlorine or bromine and ring-opening is primarily S_N2.

(b) With One Vinyl Fluorine on Carbons -1 or 2.

Halonium ions with a perfluoroalkyl group and a single fluorine on the number-2 carbon (Table 1, Run 9) appear to be nearly symmetrical (X–C₂–C₁, *ca.* 65° and X–C₁–C₂, *ca.* 73°) with the X–C₂ bond length slightly longer than X–C₁ (Tables 2 and 3, Run 9). The positive charge is greater on carbon-2 where it can be stabilized by the lone-pair of the fluorine (Table 4, Run 9). These data indicate that some Markovnikov product should be formed. Experimentally, however, only *anti*-Markovnikov was found for chlorination of 1H,1H,7H-perfluoro-heptene-1 in *tert*-butanol; only a small amount of Markovnikov product resulted from the reaction of chlorine monofluoride in methylene chloride.² The experimental product distribution for Cl₂ or ClF in solution was consistent with structure **D**.¹ We now believe that a more symmetrical

intermediate like **C** is indicated and that ring-opening of the halonium ion occurs via a S_N2 reaction at the less sterically hindered carbon-1. Bromine did not react with this electron-deficient alkene² by way of an ionic process, but we predict the products would be similar to those we found for chlorination.

A single fluorine (Table 1, Run 8) on the terminal carbon gives a less symmetrical intermediate ($X-C_2-C_1$ angle 73-80°), and the $X-C_1$ bond length is greater than $X-C_2$ (Tables 2 and 3, Run 8), the charge is positive on carbon-1 and negative on carbon-2 (Table 4, Run 8). These data suggest a unsymmetrical structure **D** (Table 1, Run 8). Experimentally we did not run a model similar to Run 8, but we anticipate substantial amounts of *anti*-Markovnikov product based on our past experimental data¹⁻⁴ and this study. This prediction is based on the intermediates slight asymmetry and the substantial positive charge on the number-1 carbon which makes nucleophilic attack on carbon-1 more like a S_N2 -like process with some S_N1 character.

(c) With Two Vinyl Fluorines. 1,1- or 1,2-Difluoroterminal Alkenes.

Our compound modeled in Run 10 has two vinyl fluorines on the terminal carbon. The halogens are above carbon-2 ($X-C_2-C_1$; $\beta > 90^\circ$), (Table 1, Run 10), and the $X-C_2$ bond is considerably shorter than $X-C_1$ bond (Tables 2 and 3, Run 10). Geometrical data and the large positive charge on carbon-1 (Table 4, Run 10) support an open-ion structure **E** for 2H-perfluoroalkenes (Table 1, Run 10). Our data predict that only *anti*-Markovnikov products would be formed from capture of the open-ions **E**.

The model in Run 11 has a fluorine on carbon-1 and on carbon-2. The bond angle (X–C₂–C₁ *ca.* 70°, Table 1), bond length (X–C₁ > X–C₂) data (Tables 2 and 3, Run 11) point to a structure close to **D**. The positive charges are also larger on carbon-1 than carbon-2 (Table 4, Run 11). This is in contrast to the halonium ions with one fluorine on each carbon when the alkyl group is a hydrocarbon (Run 5) where the positive charge is greater on carbon-2. Comparison of these two structures indicates the trifluoromethyl reduces the amount of positive charge on carbon-2, and it forces the halonium to become more symmetrical (CH₃ = **A**; CF₃ = more like **D**). Thus we would predict less **M** products from alkenes like the model in Run 11 compared to the model in Run 5. Chlorination in methanol of (E)-1H-perfluoroheptene-1 gave a substantial amount of **M** product² (Table 1, Run 11; **M:aM** 1.8:1.0). The amount of **M** product is greater than we would predict based on the symmetry and charge distribution on carbons 1 and 2. Reaction of (E)-1H-perfluoroheptene-1 was very slow and only 35 percent of the alkene reacted with chlorine after 2 days.² (E)-1H-perfluoroheptene-1 was too unreactive for bromine electrophiles, but we anticipate a similar product distribution from bromine since our calculations show that the halonium ions are similar.

(d) With Three Vinyl Fluorines. Perfluoroalkylterminal Alkenes.

The trifluoromethyl group (Table 1, Run 12) tightens the bridging in the halonium ion from the perfluoroalkene and places the halogen above carbon-2. The X–C₂ bond is considerably shorter than the X–C₁ bond, and the positive charge is greatly concentrated on carbon-1 (Tables 2, 3 and 4, Run 12). These data clearly predict nucleophilic attacks on the terminal carbon to give *anti*-Markovnikov products via intermediate **E** (Table 1, Run 12). This

structure was confirmed experimentally since only *anti*-Markovnikov products were found for ionic reaction of perfluorohheptene-1 with chlorine in a protic solvent, and from the ionic reaction of chlorine monofluoride in aprotic solvent.² Again bromine did not react by an ionic pathway.

Experimentally, perfluorovinyl ether was most interesting. In this case we experimentally assigned the intermediate structure **D** to the iodonium ion, structure **C** for the bromonium ion, and **B** for the chloronium ion.¹ Our calculations for the perfluorovinyl ether (Table 1, Run 14) are quite similar for both chloronium and bromonium ions and indicate a structure like **A**. (Table 1, Run 14). The chloronium ion has slightly more positive charge on carbon-2 than the bromonium ion, and the X–C₁–C₂, bond angle is 2 degrees larger for the chloronium ion. We suggest these calculated values are too small to account for the large change in product regioisomers for this reaction^{1,3} (Table 1, Run 14). Based on these calculations and our experimental data, we predict structure **A** for the chloronium ion and probably structure **B** for the bromonium ion since bromine bridges better than chlorine.^{1,18}

In conclusion, we have shown that calculated equilibrium geometries, bond lengths, and charge densities describe the halonium ion intermediates from ionic halogenation of terminal fluoroalkenes. These calculated data support experimental product distributions and can predict product regiochemistry from interhalogen electrophiles (XF; X=I, Br, Cl; BrCl; IBr, ICl, etc.), or from capture of the halonium ion by solvent. Electron-withdrawing alkyl groups tend to decrease the S_N1-character of the product determining ring-opening transition state and an S_N2-like process occurs which is more susceptible to steric effects.

Supporting Information Available

Data from MP2, B3LYP and B3LYP+PCM calculations are in the Supplemental Section.

This material is available free of charge via the internet at <http://pubs.acs.org>.

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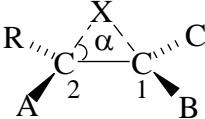
TABLE 1
Bond Angle (degrees)/Halonium Ion Structure

				B3LYP/6-311++G(d,p) + PCM(CH ₃ OH)				B3LYP/6-311++G(d,p)		MP2/6-311++G(d,p)		M/aM Experimental Product Ratio ²	Predicted Structure from Experimental ² Data CH ₃ OH		
				Structure ¹ Based on Angles				Bond Angle	Structure ¹	Bond Angle	Structure ¹				
RUN	R	A	B	C	X	X-C ₂ -C ₁	X-C ₁ -C ₂	X-C ₂ -C ₁	X-C ₁ -C ₂	X-C ₂ -C ₁	X-C ₂ -C ₁	X-C ₂ -C ₁			
1	CH ₃	H	H	H	Cl	61.2	75.7	C	B	61.7	C	64.7	C	2.6/1	B
					Br	64.3	75.8	C	B	64.3	C	62.9	C	3.1/1	
2	CH ₃	H	F	H	Cl	67.1	69.6	C⇒D	C⇒D	68.2	C⇒D	68.6	C⇒D	aM only	D
					Br	69.9	70.0	C⇒D	D⇒C	70.5	D⇒C	71.6	D⇒C	1/9.0	
3	CH ₃	F	H	H	Cl	46.3	97.9		A	49.8		55.9	C	M only	A
					Br	51.3	93.8		A	54.2		48.7		M only	
4	CH ₃	H	F	F	Cl	93.3	49.5	E		87.1	E⇒D	88.0	E⇒D	---	---
					Br	88.3	55.4	E⇒D		83.2	D⇒E	95.3	E	---	
5	CH ₃	F	H	F	Cl	44.8	93.3		A	48.9		58.2	C	---	---
					Br	51.4	93.0		A	55.4		47.1		---	
6	CH ₃	F	F	F	Cl	43.3	100.8		A	46.2		46.2		---	---
					Br	49.0	95.6		A	54.0		89.3	E⇒D	---	
7	CF ₃	H	H	H	Cl	68.6	66.1	C⇒D	C⇒B	67.9	C⇒D	67.4	C⇒D	aM only	D
					Br	70.2	68.0	D⇒C	C⇒B	69.6	C⇒D	69.4	C⇒D	aM only	
8	CF ₃	H	F	H	Cl	80.0	57.8	D	C	77.8	D	73.0	D	---	---
					Br	78.3	61.8	D	C	77.5	D	75.3	D	---	
9	CF ₃	F	H	H	Cl	63.9	72.3	C	B⇒C	61.8	C	64.9	C	aM only	D
					Br	65.9	73.5	C⇒D	B⇒C	64.4	C	66.2	C⇒D	---	
10	CF ₃	H	F	F	Cl	99.3	45.1	E		95.4	E	97.8	E	---	---
					Br	95.6	49.8	E		91.6	E	93.8	E	---	
11	CF ₃	F	H	F	Cl	75.6	60.9	D	C	71.5	D⇒C	70.0	D⇒C	1.8/1 ³	C
					Br	73.2	65.8	D⇒C	C⇒B	71.8	D⇒C	71.5	D⇒C	---	
12	CF ₃	F	F	F	Cl	99.4	44.2	E		95.4	E	98.8	E	aM only	E
					Br	94.4	49.9	E		89.3	D⇒E	92.4	E	---	
13	CH ₃ O	H	H	H	Cl	41.9	105.0		A	46.0		45.5		M only ⁴	A ⁴
					Br	46.5	100.9		A	49.8		45.6		M only ⁴	
14	CF ₃ O	F	F	F	Cl	40.3	105.4		A	41.0		40.6		2.4/1	B
					Br	43.6	103.4		A	44.6		43.8		1/4.7	
15	Br(CH ₂) ₂	F	F	F	Cl	43.1	101.0		A	45.2		44.9		1/2.1	C
					Br	50.5	93.4		A	52.4		92.5	E	1/1.3 ⁵	

¹The symbol ⇒ means becomes like. For example: C⇒B means the structure resembles C but contains some of the symmetry is structure B. It resembles C more than B. The structure not assigned when the angle is around 55 degrees or less. ²Structures assigned from experimental data in reference 1 unless noted. ³Experimental data from reference 2.

⁴Unpublished data. ⁵The product ratios in reference 1 were influenced by the 1,2,4-tribromo-1,1,2-trifluorobutane product overlapping the aM product in the gas chromatograph. A more accurate M/aM product ratio of 1:1.3 was obtained by ¹⁹F NMR.

TABLE 2
Bond Lengths (Angstroms)

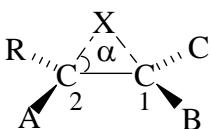


 B3LYP/6-311++G(d, p) + PCM(CH₃OH)

B3LYP/6-311++G(d, p) (Gas Phase)

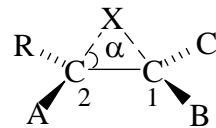
RUN	R	A	B	C	X	Predicted Structures					PCM					B3LYP/6-311++G(d, p) (Gas Phase)				
						C ₁ -C ₂	C ₁ -X	C ₂ -X	C ₁ -F _B	C ₁ -F _C	C ₂ -F _A	C ₁ -C ₂	C ₁ -X	C ₂ -X	C ₁ -F _B	C ₁ -F _C	C ₂ -F _A			
1	CH ₃	H	H	H	Cl	1.456	1.867	2.065	---	---	---	C \Rightarrow B	1.460	1.865	2.043	---	---	---		
					Br	1.448	2.021	2.114				C \Rightarrow B	1.454	2.020	2.169					
2	CH ₃	H	F	H	Cl	1.453	1.952	1.985	1.306	---	---	C \Rightarrow D	1.458	1.967	1.968	1.298	---	---		
					Br	1.445	2.112	2.114	1.308			D \Rightarrow C	1.452	2.122	2.107	1.302				
3	CH ₃	F	H	H	Cl	1.473	1.820	2.495	---	---	1.277	A	1.469	1.824	2.386	---	---	1.282		
					Br	1.457	1.984	2.538			1.286	A	1.456	1.989	2.454			1.290		
4	CH ₃	H	F	F	Cl	1.471	2.425	1.846	1.254	1.255	---	E	1.466	2.312	1.862	1.263	1.263	---		
					Br	1.454	2.455	2.022	1.264	1.264		E \Rightarrow D	1.453	2.360	2.040	1.273	1.272			
5	CH ₃	F	H	F	Cl	1.498	1.800	2.522	---	1.347	1.269	A	1.491	1.813	2.402	---	1.335	1.278		
					Br	1.478	1.980	2.531		1.340	1.279	A	1.474	1.999	2.421		1.329	1.289		
6	CH ₃	F	F	F	Cl	1.526	1.783	2.555	1.325	1.329	1.262	A	1.519	1.794	2.472	1.316	1.324	1.269		
					Br	1.506	1.965	2.590	1.322	1.325	1.270	A	1.495	1.993	2.463	1.310	1.317	1.280		
7	CF ₃	H	H	H	Cl	1.454	1.905	1.871	---	---	---	C \Rightarrow D	1.458	1.902	1.889	---	---	---		
					Br	1.451	2.047	2.018				D \Rightarrow C	1.453	2.047	2.035					
8	CF ₃	H	F	H	Cl	1.457	2.133	1.832	1.271	---	---	D	1.459	2.097	1.847	1.277	---	---		
					Br	1.452	2.213	1.991	1.283			D	1.453	2.205	2.004	1.286				
9	CF ₃	F	H	H	Cl	1.450	1.879	1.994	---	---	1.290	B \Rightarrow C	1.455	1.869	2.047	---	---	1.285		
					Br	1.445	2.026	2.129			1.297	B \Rightarrow C	1.450	2.023	2.170			1.293		
10	CF ₃	H	F	F	Cl	1.482	2.507	1.798	1.245	1.246	---	E	1.476	2.438	1.807	1.255	1.252	---		
					Br	1.464	2.563	1.966	1.252	1.253		E	1.460	2.491	1.978	1.263	1.259			
11	CF ₃	F	H	F	Cl	1.472	2.068	1.865	---	1.274	1.311	D	1.474	2.011	1.915	---	1.282	1.303		
					Br	1.467	2.143	2.043		1.289	1.310	D \Rightarrow C	1.469	2.135	2.074		1.291	1.307		
12	CF ₃	F	F	F	Cl	1.517	2.520	1.781	1.239	1.241	1.334	E	1.511	2.453	1.795	1.249	1.249	1.329		
					Br	1.495	2.554	1.959	1.246	1.248	1.332	E	1.488	2.463	1.982	1.258	1.259	1.326		
13	CH ₃ O	H	H	H	Cl	1.477	1.808	2.615	---	---	---	A	1.475	1.813	2.496	---	---	---		
					Br	1.467	1.973	2.671				A	1.464	1.977	2.575					
14	CF ₃ O	F	F	F	Cl	1.543	1.768	2.637	1.329	1.326	1.265	A	1.548	1.768	2.616	1.327	1.323	1.275		
					Br	1.532	1.941	2.738	1.329	1.327	1.267	A	1.533	1.942	2.707	1.326	1.323	1.276		
15	Br(CH ₂) ₂	F	F	F	Cl	1.527	1.781	2.558	1.325	1.328	1.262	A	1.521	1.793	2.504	1.318	1.325	1.273		
					Br	1.503	1.972	2.549	1.319	1.322	1.271	A	1.499	1.986	2.506	1.313	1.319	1.281		

TABLE 3
Bond Lengths (Angstroms)


MP2/6-311++G(d,p) (Gas Phase)

RUN	R	A	B	C	X	C ₁ -C ₂	C ₁ -X	C ₂ -X	C ₁ -F _B	C ₁ -F _C	C ₂ -F _A
1	CH ₃		H	H	Cl	1.462	1.842	1.909	---	---	---
					Br	1.441	2.012	2.205			
2	CH ₃	H	F	H	Cl	1.457	1.920	1.890	1.298	---	---
					Br	1.436	2.129	2.089	1.273		
3	CH ₃	F	H	H	Cl	1.458	1.815	2.174	---	---	1.284
					Br	1.463	1.958	2.587			1.249
4	CH ₃	H	F	F	Cl	1.461	2.294	1.821	1.257	1.257	---
					Br	1.464	2.564	1.973	1.229	1.229	
5	CH ₃	F	H	F	Cl	1.470	1.831	2.112	---	1.317	1.288
					Br	1.486	1.939	2.615		1.317	1.243
6	CH ₃	F	F	F	Cl	1.513	1.762	2.429	1.315	1.322	1.260
					Br	1.473	2.151	2.104	1.279	1.284	1.311
7	CF ₃	H	H	H	Cl	1.461	1.858	1.839	---	---	---
					Br	1.458	2.020	2.002			
8	CF ₃	H	F	H	Cl	1.456	1.975	1.826	1.284	---	---
					Br	1.454	2.144	1.988	1.288		
9	CF ₃	F	H	H	Cl	1.455	1.853	1.921	---	---	1.294
					Br	1.453	2.011	2.095			1.297
10	CF ₃	H	F	F	Cl	1.476	2.459	1.776	1.248	1.245	---
					Br	1.460	2.519	1.958	1.254	1.251	
11	CF ₃	F	H	F	Cl	1.469	1.948	1.878	---	1.285	1.298
					Br	1.467	2.108	2.048		1.289	1.301
12	CF ₃	F	F	F	Cl	1.512	2.486	1.756	1.240	1.241	1.333
					Br	1.488	2.502	1.951	1.249	1.250	1.329
13	CH ₃ O	H	H	H	Cl	1.476	1.784	2.474	---	---	---
					Br	1.475	1.946	2.669			
14	CF ₃ O	F	F	F	Cl	1.540	1.740	2.590	1.325	1.322	1.269
					Br	1.531	1.921	2.707	1.325	1.322	1.270
15	Br(CH ₂) ₂	F	F	F	Cl	1.514	1.756	2.465	1.319	1.327	1.266
					Br	1.473	2.140	2.112	1.281	1.286	1.312

TABLE 4
Charge Densities

ATOMIC CHARGES – PCM¹ATOMIC CHARGES – MP2²

RUN	R (Rc)	A	B	C	HALOGEN	Predicted Structures PCM				Predicted Structures MP2						
						C ₁	C ₂	C ₃	X	C ₁	C ₂	X	F _C	F _B	F _A	
1	CH ₃	H	H	H	X = Cl	0.24	-0.15	0.09	0.35	C \Rightarrow B	0.258	-0.043	0.406			
					X = Br	-0.04	0.03	-0.20	0.38	C \Rightarrow B	0.313	0.134	0.307			
2	CH ₃	H	F	H	X = Cl	0.07	-0.02	-0.19	0.41	C \Rightarrow D	0.373	-0.124	0.363	-0.256		
					X = Br	0.10	0.00	-0.19	0.40	D \Rightarrow C	0.482	-0.098	0.294	0.315		
3	CH ₃	F	H	H	X = Cl	-0.16	0.20	-0.15	0.23	A	-0.394	0.700	0.251			-0.240
					X = Br	-0.09	0.17	-0.16	0.24	A	-0.524	0.978	0.191			-0.303
4	CH ₃	H	F	F	X = Cl	0.21	-0.13	-0.19	0.27	E	1.072	-0.296	0.188	-0.194	-0.190	
					X = Br	0.18	-0.07	-0.19	0.30	E \Rightarrow D	1.294	-0.381	0.194	-0.262	-0.260	
5	CH ₃	F	H	F	X = Cl	-0.06	0.21	-0.15	0.28	A	0.217	0.623	-0.275	-0.278		-0.241
					X = Br	0.30	0.17	-0.16	0.29	A	0.111	0.964	-0.187	-0.355		-0.291
6	CH ₃	F	F	F	X = Cl	-0.06	0.22	-0.13	0.34	A	0.624	0.775	0.175	-0.293	-0.284	-0.186
					X = Br	0.02	0.19	-0.14	0.34	A	0.623	0.696	0.270	-0.240	-0.230	-0.269
7	CF ₃	H	H	H	X = Cl	0.00	-0.04	0.09	0.57	C \Rightarrow D	-0.224	-0.196	0.489			
					X = Br	0.02	0.00	0.09	0.54	D \Rightarrow C	-0.281	-0.251	0.604			
8	CF ₃	H	F	H	X = Cl	0.19	-0.11	0.09	0.47	D	0.431	-0.281	0.410		-0.230	
					X = Br	0.16	-0.04	0.09	0.48	D	0.398	-0.348	0.517		-0.234	
9	CF ₃	F	H	H	X = Cl	-0.03	0.05	0.10	0.52	B \Rightarrow C	-0.295	0.425	0.436			-0.245
					X = Br	0.00	0.07	0.10	0.52	B \Rightarrow C	-0.367	0.395	0.543			-0.249
10	CF ₃	H	F	F	X = Cl	0.24	-0.15	0.09	0.35	E	1.134	-0.436	0.198	-0.158	-0.163	
					X = Br	0.21	-0.07	0.09	0.36	E	1.089	-0.495	0.325	-0.172	-0.179	
11	CF ₃	F	H	F	X = Cl	0.16	-0.04	0.09	0.53	D	0.361	0.335	0.393	-0.227		-0.245
					X = Br	0.14	0.03	0.09	0.53	D \Rightarrow C	0.312	0.294	0.497	-0.232		-0.249
12	CF ₃	F	F	F	X = Cl	0.24	-0.10	0.08	0.41	E	1.106	0.143	0.204	-0.150	-0.145	-0.286
					X = Br	0.20	-0.01	0.08	0.40	E	1.045	0.106	0.331	-0.167	-0.164	-0.281
13	CH ₃ O	H	H	H	X = Cl	-0.19	0.17	0.04	0.15	A	-0.446	0.499	0.101			
					X = Br	-0.11	0.14	0.03	0.14	A	-0.502	0.666	0.134			
14	CF ₃ O	F	F	F	X = Cl	-0.05	0.18	0.07	0.33	A	0.610	0.937	0.139	-0.292	-0.294	-0.202
					X = Br	0.04	0.17	0.07	0.29	A	0.560	0.926	0.216	-0.293	-0.294	-0.203
15	Br(CH ₂) ₂	F	F	F	X = Cl	-0.06	0.22	-0.15	0.35	A	0.620	0.756	0.170	-0.301	-0.289	-0.196
					X = Br	0.04	0.17	-0.16	0.35	A	0.637	0.664	0.298	-0.243	-0.233	-0.270

¹Lodwin atomic charges from the B3LYP/6-311++G(d,p)+PCM calculations. ²Natural Population Analysis charges from the MP2/6-311++G(d,p) calculations.